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I, KIM MARSHALL, MANAGER EXAMINATION SUPPORT AND SALES, hereby certify that the annexed is a true copy of the Provisional specification in connection with Application No. PP 4550 for a patent by COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION filed on 7 July 1998.

WITNESS my hand this Twenty-ninth day of July 1999

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PROVISIONAL SPECIFICATION

Applicant(s):

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL
RESEARCH ORGANISATION

Invention Title:

PROCESS FOR CHLORINE RECOVERY

The invention is described in the following statement:

PROCESS FOR CHLORINE RECOVERY

The present invention is concerned with a process
for the recovery of chlorine from metal chlorides. More
specifically, the invention relates to a process for
dechlorinating iron chloride mixed with several other metal
chlorides to produce chlorine gas. The process has the
ability to recover chlorine from these chlorides in the
presence of carbon and other materials such as oxides which
are present in typical wastes generated during the
chlorination of synthetic rutile.

Titanium tetrachloride is conventionally produced
from either ilmenite or rutile (including synthetic rutile)
in a fluidised bed at around 1000°C. Chlorine, a carbon
rich material such as petroleum coke and a titanium-bearing
material are fed into the fluidised bed chlorinator and
titanium tetrachloride vapour leaves the system in the gas
phase. It is subsequently condensed, purified and used in
the production of either pigment or titanium metal.
Chlorine is recycled to the chlorinator.

Impurities such as Mg, Mn, Al in the feed are
chlorinated to varying degrees. Iron in the feed
chlorinates readily and is sufficiently volatile to leave
the reactor with the effluent gas. It condenses from the
gas phase at temperatures around 300°C, compared to
titanium tetrachloride which condenses to a liquid at about
100°C. Iron chloride is therefore amenable to separation by
differential condensation. It is recovered as a solid in
the chlorinator off gas cooling system.

The condensed stream from the chlorinator typically contains chlorides such as $FeCl_2$, $MnCl_2$, $MgCl_2$ and $AlOCl$, as well as large quantities of coke and synthetic rutile which are blown over from the chlorinator. This

5   material is referred to as the chlorinator waste.

The chlorinator waste is subsequently disposed of by whatever means are most acceptable from an environmental point of view. Techniques include direct dumping in

10   mineshafts, blending into concrete for low-strength marine applications and wet chemical treatment to produce iron oxide and HCl (or NaCl with usage of caustic soda). In some pigment plants the waste is currently disposed of by mixing it with CaO and water which react with the chlorides to

15   form oxides and $CaCl_2$. The oxides and other solids are thickened, de-watered and returned to the mine. The $CaCl_2$ liquor is discharged into the ocean.

These forms of disposal mean that valuable

20   chlorine present as chlorides in the chlorinator waste is not recovered. These options are also undesirable because they are either environmentally sensitive or costly in terms of consumables and generally call for minimisation of iron chloride production. For this reason, rutile is the

25   feedstock of choice for chlorination. It contains less iron than ilmenite. In commercial processes, therefore, ilmenite is first converted to synthetic rutile by removing substantially all of the iron by appropriate pre-treatment processes and the synthetic rutile is subsequently used in

30   the chlorination process.

An alternative to simply disposing of the chlorinator waste is to react the waste directly with

oxygen to form oxides and recover the chlorine as shown schematically in Figure 1. The oxides generated could be useful as landfill or smelter feed, or returned to the mine and the chlorine recycled to the chlorinator. Such a

5   dechlorination process has the potential to reduce the cost of pigment production by reducing the quantity of fresh chlorine required, and by significantly reducing the consumption of water.

10   The chlorination industry has a long-standing need for a process which can convert iron chloride into chlorine and iron oxide. In the production of titanium tetrachloride the chlorine could be directly recycled to the chlorinator, thereby decreasing the need for chlorine-

15   make-up. For such a process to be effective, the iron oxide produced would need to be sufficiently free of chlorine to allow disposal as landfill or smelter feed with little or no further treatment. The availability of such a process would create the potential for:

20

Direct chlorination of ilmenite in the case of "clean" (low Ca, Mg, Mn, Al) deposits. This simultaneously obviates the need for synthetic rutile production and offers a solution to the iron chloride disposal problem.

25

Ilmenite conversion to synthetic rutile by partial chlorination with subsequent alkali removal in the case of dirty (high Ca, Mg and/or Mn) deposits. This would present an alternative to more conventional methods of

30   impurity removal by reduction and leaching and would lead to reduced waste disposal requirements.

A general waste disposal route for undesired iron chloride and other chlorides which yields chlorine for direct recycle to chlorination systems. This includes the use of skid mounted plants to process accumulated iron

5   chloride waste at existing chlorinator sites, particularly in Europe and USA.

Prior art

10   The proposed technologies for chlorine recovery, as disclosed in the literature, are not sufficiently selective and/or have unattractive scale-up features.

The Du Pont recirculating fluidised bed approach
15   (US patents 3793444, 4144316 and 4174381) claims greater than 95% chlorine removal, leaving a nominal 3-5% leachable chloride in the solid phase and rendering it unsuitable for direct disposal.

20   The Mitsubishi vapour-phase approach (S Fukushima and Y. Sugawara, Light metals, AIME 1974), claims 90% chlorine removal and in addition, has perceived scale-up limitations.

25   The Mineral Process approach (US patent 4140746) involves a reduction step for partial dechlorination of ferric chloride, followed by an oxidative step yielding chlorine, iron oxide and ferric chloride which must then be recycled. Besides being fairly complex, it does not offer
30   good potential for a "clean" iron oxide waste stream.

SCM Chemical's US patent 4624843 (inventor M Robinson, 25 Nov 1986) refers to control of the proportions

of the iron chloride and carbon in the blown over material from the chlorinator by controlling the iron oxide concentration in the feed to the chlorinator. The iron oxide is claimed to be introduced through the addition of

5   ilmenite and/or rutile slag. The chlorinator is therefore being used as a selective chlorinator or beneficiator to upgrade other Ti bearing materials. The blown over carbon is controlled between 7.5 and 20% carbon based on the carbon plus iron chloride only, the blow over of rutile is

10   not specifically mentioned. It is claimed that the iron chloride is formed as ferric chloride under the conditions used in the selective chlorinator but this cannot be verified in the absence of sufficient information in the patent. This does not agree with our observation of

15   chlorinator waste which show that iron is almost completely present as ferrous chloride as discussed below.

       The dechlorinator claimed in US patent 4624843 is based on the introduction of more than one oxygen

20   streams into the reactor. A first stream introduced at the base of the fluidised bed is intended to react with the carbon content of the feed and maintain the bed temperature at between 500 and 1050°C, "preferably at least at 600°C". This step seems to be intended to vaporise the ferric

25   chloride although the patent is not very clear on this aspect. A second or more oxygen streams, which appear to need preheating, are introduced above the bed to react with the ferric chloride vapour.

30   With the dechlorination reaction occurring in the gas phase above the bed between ferric chloride vapour and oxygen, the conversions are unlikely to be complete because of residence time constraints. This implies that iron

chloride recycle levels will be significant. Moreover, the
iron oxide will be produced as fine dust which increase the
probability of accretion formation at the bed exit.

5   We have discovered that waste obtained from
typical chlorinators a) the iron is present as <u>ferrous</u>
chloride, b) the conversion of ferrous to ferric chloride
is reasonably rapid during dechlorination and c) the
conversion of chloride to oxide is helped by using a
10   fluidised bed of particles. The need for the type of pseudo
multi-stage operation claimed in US patent 4624843 makes
reactor operation and control more difficult with no
perceived gain.

15   SCM Chemicals' US patent 4994255 (inventor C K
Hahn, 19 February 1991) is a process patent which claims
several hypothetical process schemes in which a major
feature is the claim to apparent complete or near complete
separation of carbon from the rest of the blown over
20   material. It is claimed that "the carbon and ore solids can
be most efficiently removed by using a ceramic filter bag
in a baghouse. The temperature can be as high as 800°C."
However, the patent goes on to state that the "carbon
content in the condensed $FeCl_2$ under these conditions is
25   below about 12% and usually, the removal of carbon and ore
is <u>almost</u> complete". The patent also refers to US patent
4094954 and states that "the carbon, together with any ore
in the offgas stream can be separated by conventional means
such as using a hot cyclone separator, electrostatic
30   separator or a knock-out pot. Their claim implies,
erroneously, that at 800°C the ferrous chloride is in
vapour form.

The conceptual flowsheets in figures 1,2,4 and 5 in US patent 4994255 are not substantiated by any results. It is clear from the descriptions and diagrams that the patent assumes that substantially pure $FeCl_2$ is treated in

5   the $FeCl_2$ oxidiser. The $FeCl_2$ oxidiser appears to be based on an inert material which is partly removed with the iron oxide coating. Because their patent is based on pure or substantially pure iron chloride, an inert bed is necessary to avoid potential problems due to molten chloride.

10

US patent 4994255 does not reveal the optimum operating conditions such as temperature and oxygen/waste feed ratio for maximum chlorine recovery at economic rates of chlorine production other than to say that the

15   temperature should be below the melting point of $FeCl_2$ (674°C).

We have discovered that in a real chlorinator waste the conversion rates of the chlorides can be quite

20   rapid despite the presence of liquid phases which melt at much lower temperatures when other metal chlorides such as those of Mn and Mg are present along with iron chloride. Our invention is not limited to pure iron chloride.

25   US patent 4144316 for <u>ferric</u> chloride conversion claims the need to add a catalyst (sodium chloride) to achieve satisfactory conversion in a fluidised bed of ferric chloride particles. US patent 3944647, restricted to the treatment of <u>ferric</u> chloride, also claims the use of

30   sodium chloride to produce a liquid sodium ferric chloride salt complex which is subsequently reacted with oxygen.

Various publications have dealt with the problems of obtaining high conversions with ferric chloride. A paper by Olsen (Olsen R S, in Recycle and Secondary recovery of metals, 1985, Taylor P R et al editors, pp771-783) gives

5   results of a preliminary study of the treatment of ferrous chloride in a fluidised bed but the reported conversions were low. We have discovered that in a real chlorinator waste, the conversion rate and final conversion of the chlorides in the waste are high without the need for any

10   catalyst addition.

US patent 3642441 (Falconbridge Nickel Mines) appears to be based on a complex process with a multiplicity of streams and relies on the endothermic

15   reaction of "explosive" mixtures of metal chlorides with water and combustion of the mixtures. Significant quantities of hydrogen bearing gases will result and even if the process were capable of being scaled up satisfactorily, it is likely to be more suited to HCl

20   rather than chlorine production.

US patent 3325252, and related US patent 3050365, are based on a two-zone furnace using molten iron chloride feed. Based on the quoted example,

25   liquid ferric chloride is fed under pressure through a spray head to the inner tube of a burner with oxygen supply through an outer tube. It is claimed that the reaction is completed in a second, lower zone, into which alumina particles are fed. This zone was maintained at about 450°C

30   but the rate of chlorine recovery would have been low under these conditions. The process seems to be restricted to iron chloride levels less than 10% in the feed. Higher ferrous chloride levels are unlikely to give satisfactory

chlorine recoveries because of short residence times and the absence of inert substrate particles in the upper zone and the slow kinetics in the lower zone. Accretion formation is also seen as a major problem. US patent
5   3092456 attempts to address this issue but a practical solution is not simple.

The vapour phase contacting method claimed by Mitsubishi (US patent 4073874 to Fukushima et al) is based
10   on treating <u>ferric</u> chloride. The ferric chloride vapour and several streams of oxygen, injected through nozzles, reacting with each other in an enclosure. It is claimed that in initial work there were significant operational problems caused by the formation of iron oxide accretions
15   at the point where the chloride vapour stream impinged on the oxygen stream. It appears that the problem (Fukushima S and Sugawara Y in Light Metals Technology II, 1974, pp443-466) with accretions was not completely eliminated.

20   In summary, the application of fluidised bed or other (mainly vapour phase contacting with oxygen) technologies to the recovery of chlorine from iron chloride has been the subject of a few patents and literature but these claimed processes have severe limitations that have
25   apparently hindered successful commercial implementation.

Processes based on direct gas phase contacting between iron chloride vapour and oxygen in the absence of a bed of inert material have significant problems due to
30   accretion formation resulting from the production of fine dust of iron oxide.

Beneficiation/partial chlorination in which iron units are added through ilmenite or rutile based slag to control the carbon/chloride ratio in the waste is impractical because control of the waste composition to
5 optimise the dechlorination unit cannot be achieved as indicated in US patent 4624843.

Pre-oxidation of the waste to 500-800°C (US patent 4060584) to apparently convert the ferrous chloride
10 to ferric chloride vapour and iron oxide, the ferric chloride vapour being separated from the iron oxide using high temperature separation and subsequently dechlorinating the iron chloride vapour in a multi stage process will not recover the significant amount of chlorine associated with
15 the other metals which will stay with the solids in the pre-oxidiser.

It is also important to note that the patents ignore the fact that the chlorine associated with iron is
20 only a proportion of the total chlorine available for recovery and the chlorine associated with, the other elements such as Mn, Mg and Al and other elements need to be recovered.

25 We note that carbon and ore blow through occurs routinely in synthetic rutile chlorination plants and recognise that it is difficult to eliminate such blow through and/or implement cost-effective technology for separating the carbon and ore from the chlorides at the
30 exit of the chlorinator. We have also discovered that the major amount of chloride collected in the blown over material is coated on the larger carbon and rutile particles with a minor amount as free chlorides. It is

therefore important to recover the chlorine from the chloride coated on the particles and it is not sufficient to remove the carbon and rutile particles by filtration or other means as has been proposed in some of the prior art

5   discussed above.

According to a first aspect of the present invention there is provided a process for recovering chlorine from chlorinator waste, comprising the steps of:

10

     (1)   providing a fluidised bed comprising chlorinator waste and oxygen or an oxygen-containing gas; and

15   (2)   allowing oxidation of chlorides in said chlorinator waste to occur within said fluidised bed.

Preferably the process further comprises the
20   steps of separately recovering metal oxides and chlorine gas. Typically the chlorine gas is recycled into the chlorinator in a process for the production of titanium tetrachloride from ilmenite or rutile, including synthetic rutile.

25

Typically the chlorinator waste contains chlorides such as $FeCl_2$, $MnCl_2$, $MgCl_2$, $AlOCl$, as well as large quantities of coke and feed material such as synthetic rutile which are blown over from the chlorinator
30   in a process for production of titanium tetrachloride. Accordingly, in a preferred embodiment of the invention the dechlorination of the chloride is achieved by controlling the temperature within said fluidised bed, the oxygen to

chlorinator waste feed ratio and superficial velocity of the gas in the fluidised bed, either separately or in combination, so as to maximize the recovery of chlorine gas and/or minimize the conversion of carbon. Under these

5   conditions the dechlorination process strips chlorine absorbed to particulate matter in the feed, such as carbon and rutile particles, and from separate chloride particles in the feed.

10   Preferably the temperature in the fluidised bed is in the range of 550 to 700°C, the superficial velocity of the gas is in the range of 0.2 to 1.0 m/s and the oxygen to chlorinator waste feed molar ratio is in the range 0.2 to 0.8. Typically the temperature in the fluidised bed

15   reactor, the superficial velocity of the gas and the oxygen to waste molar ratio can be selected depending on the composition and morphological characteristics of the chlorides and other particles, including the particle size of the particles, in the chlorinator waste.

20

         According to a second aspect of the present invention there is provided an apparatus for recovering chlorine from chlorinator waste, comprising a fluidised bed reactor; means for introducing chlorinator waste into said

25   fluidised bed reactor; and means for introducing oxygen or an oxygen-containing gas into said fluidised bed reactor; said fluidised bed reactor including means for controlling the temperature, the oxygen to chlorinator waste feed ratio and the superficial velocity of the gas in the reactor,

30   either separately or in combination so as to maximize chlorine gas recovery and/or minimize the conversion of carbon.

In a preferred embodiment of the invention the fluidised bed reactor has a conical bottom entry region for the chlorinator waste feed material and oxygen. The reactor is appropriately water cooled or heated to allow

5   the extraction or addition of heat to the process depending on the energy requirement of the process, which can be calculated based on the waste composition and the operating parameters.

10   In another embodiment, the fluidised bed reactor includes a distributor plate to feed the gas into the bed.

According to a third aspect of the present invention there is provided a system for recovering

15   chlorine from chlorinator waste including the apparatus described above, and further comprising means for collecting particulate matter which leave the fluidised bed reactor and means for quenching any unreacted chlorinated compounds which leave the fluidised bed reactor.

20

Typically the means for collecting particulate matter is a cyclone and the means for quenching unreacted chlorinated compounds is a quencher downstream of the cyclone. In this arrangement solid materials are collected

25   in the cyclone and the resultant gas stream passed through the quencher. The quencher is arranged so that condensable vapors are removed by quenching and the chlorine gas stream that results is conveyed to a baghouse or other appropriate separation device to remove any residual fine dust

30   particles so as to obtain a clean chlorine gas stream. The chlorine gas stream can be directed to a chlorinator in a titanium tetrachloride production process.

Preferably the cyclone is maintained at a temperature above the condensation temperature of any unreacted chlorinated compounds so that an effective separation is achieved between the solids and the unreacted

5   chlorinated compounds. Typically the conditions in the cyclone, including the residence time of the particles and the temperature in the cyclone are chosen so as to avoid oxidation of carbon in the cyclone.

10   According to a fourth aspect of the present invention there is provided a process for the dechlorination of metal chlorides in a mixture including at least one metal chloride and also including carbon, or carbon, and other materials such as, but not limited to,

15   metal oxides, comprising the steps of:

(1)   providing a fluidised bed comprising said mixture and oxygen or an oxygen-containing gas; and

20

(2)   allowing oxidation of the metal chlorides to occur within said fluidised bed.

Typically the mixture contains ferrous and/or

25   ferric chloride and chlorides such as those of manganese, magnesium, calcium and aluminium. The mixture may also include metal chlorides such as those of V, Cr, Mb, Zr, Na, Ba, Ce, Sr, Si, Be or Cu.

30   Preferred embodiments of the present invention will be described, by way of example only, with reference to the accompanying figures, in which:

Fig 1 is a flow chart illustrating the general process for preparation of titanium dioxide pigment from synthetic rutile, including treatment of the chlorinator waste.

5

Fig 2 shows a back scatter electron image of (a)a synthetic rutile particle and (b) a carbon particle typical of those present in a sample of blown over material from an operating chlorinator in the process schematically

10   illustrated in Fig 1.

Fig 3 is a graph of fraction of chlorine present as certain chosen species verses temperature for a thermodynamic simulation of the effect of temperature on

15   the distribution of Cl between species and R equals 0.96. The fraction of Cl associated with the species is graphed on the primary Y axis and the fraction of Cl_2 gas recovery on the secondary X axis.

20   Fig 4 is a graph of the fraction of Cl present as certain species verses the input of oxygen gas in a thermodynamic simulation of the effect of O_2 on the distribution of Cl between species at 650°C.

25   Fig 5 is a schematic diagram of a dechlorination facility capable of use in the present invention.

Fig 6 is a schematic diagram of the overall process.

30

By way of explanation of the invention we illustrate in Figure 2 typical back scatter electron images of (a) a synthetic rutile particle and (b) a carbon

particle typical of those present in a sample of blown over
material from an operating chlorinator. The images show
that the condensed chlorides were present as a coating,
about 10μm thick on the surface and in the external pores

5   of the particles. Both images also show small, separate
agglomerates 1 to 10 μm of chlorides. Based on examination
of the sample under the SEM and microprobe, it appears that
about half of the condensed chlorides was present on the
particles and the other as agglomerates. It is clear form

10 the nature of the coating on the surface of the rutile and
coke particles that the particles cannot be easily
separated from the chlorides and returned to the
chlorinator.

15   It is important to note that typical samples
contained a large number of elements in significant
quantities, as chlorides and oxides. Typical concentrations
of various species are given in Table 1.

20   It is noteworthy that the composition of typical
waste from a chlorinator is quite different from the simple
iron chloride material considered in the prior art.   It is
also noteworthy that typical waste does not contain any
significant quantity of _ferric_ chloride.   The major

25 chloride bearing species is ferrous chloride. The large
number of chloride and oxide species is particularly
noteworthy. The sample also contains a significant amount
of carbon, about 23% carbon in the example in Table 1.
Prior art does not reveal the conditions required to

30 maximize chlorine recovery _and_ minimize carbon combustion
from this type of complex material to obtain chlorine gas
with practically relevant concentrations.

By way of the basis for our process we illustrate in Figure 3 the thermodynamic simulation of the results of dechlorination showing the effects of temperature at a constant molar ratio, R, of oxygen:waste = 0.96. Increasing

5   the temperature decreases the recovery of chlorine due to the increased stability of the chlorides at the higher temperature. At temperatures below 150°C, the only chlorides that do not release chlorine are those of Ba, Na and Nb. At 150°C, VCl_3 reacts with oxygen and its

10   conversion to the oxide is complete at about 400°C. The chloride of chromium also reacts at about 150°C and its conversion via the oxychloride is complete at about 700°C. At 650°C, $MnCl_2$ forms a liquid at the expense of Mn_2O_3. As the temperature increases to 1000°C, ferric chloride,

15   ferrous chloride, manganese chloride and niobium oxychloride increase at the expense of oxides. From 100 to 1000°C, the removal of chlorine from $AlCl_3$ and $MgCl_2$ is complete while NaCl remains unreacted.

20

Table 1.   Composition of a chlorinator waste

Species	Concentration (wt%)
$FeCl_2$	12.4
AlOCl	3.8
$MnCl_2$	3.9
$MgCl_2$	2.2
$TiCl_4$	0.35

V,Cr,Ca, Nb,Zr, Na, Ba, Ce, Sr, Si, Be, Cu chlorides	1.6
TiO$_2$	46.1
SiO$_2$	2.1
Oxides of Nb,Al,Cr, V,Zr,Cu, Fe,Ce,Ba, Mg,Mn,Ca,Be,Sr ,Na	3.2
Carbon	23.2
Sulphur	1.1

With increase in temperature the overall equilibrium conversion to chlorine gas decreases but the

5   rates of the various dechlorination reactions increase. These results and our observations show that at higher temperatures where the dechlorination kinetics of ferric chloride are acceptable, a proportion of the iron chloride and manganese chloride remain unreacted and the overall

10   chlorine recovery drops significantly with increase in temperature above about 750°C.

Figure 4 shows that at a constant temperature of 650°C, increasing the quantity of oxygen increases the

15   recovery of chlorine when thermodynamic equilibrium prevails. Below about 70 moles of oxygen per 100 moles of waste, most of the chlorides remain unreacted due to the

preferential consumption of oxygen for the oxidation of carbon. It is clear that above about 85 moles of oxygen per 100 moles of waste, there is no significant increase in the recovery of chlorine.

Results typically as illustrated above clearly show that it is necessary to maximize the recovery of chlorine while minimising the combustion of carbon in order to obtain a chlorine-rich gas and minimize the oxygen consumption.

We have discovered that the carbon combustion can be significantly reduced by the appropriate selection of temperature, gas superficial velocity in the dechlorination reactor and the stoichiometric ratio, R, defined as the moles of oxygen per mole of waste fed to the reactor.

A dechlorination facility as illustrated schematically in Figure 5 was used to demonstrate our process. It should be noted that the specific scheme shown in the figure is only indicative of the process used to demonstrate our invention and is not intended to be limiting of the invention in any way, the major purpose of the experimental scheme being the demonstration of the selectivity which was achieved with respect to maximizing chlorine recovery and minimising carbon combustion.

The system used to demonstrate the process comprises a feed hopper 11, an inlet 12 for chlorinator waste and a vent 13. The feed hopper 11 has an outlet 14 which includes an inlet 15 for dry nitrogen and an inlet 16 for oxygen, and hence a mixture of chlorinator waste and an oxygen-containing gas is fed along line 17 to the

chlorinator 20. The chlorinator waste is fed into the
bottom of the fluidised bed reactor 20 through a conical
entry 21 which allows the waste to be injected into the bed
in a controlled and reproducible manner. In the

5   experiments conducted the bed material was initially rutile
which was gradually replaced by the waste material as the
test progressed. The bed height was maintained at a
constant value by periodically withdrawing accumulated
material from the reactor 20. The reactor 20 includes

10 provision to extract or supply heat, in this case cooling
the inlet 22 and water cooled jacket 23, as desired to
maintain the temperature of the reactor and the fluidised
bed at the selected value. Appropriate temperature
measurement devices 24 and pressure measurement devices 25

15 are included.

        The fluidised bed reactor 20 includes an outlet
26 for a chlorine-rich gas stream leaving the reactor. The
chlorine-rich gas stream is then treated to remove any

20 contaminants from the chlorine gas, first by being passed
through cyclone 30 which separates particulate matter from
the gas stream, then through filter 31 which removes
further small particles from which gas stream 32 emerges
which contains chlorine, carbon dioxide and oxygen. This

25 gas stream could be treated if required to increase the
chlorine concentration further. In some tests a quencher
(not shown) was used before the filter to quench any
unreacted chloride vapors.

30   With this experimental system we achieved
independent and careful control of the temperature of the
reaction, the oxygen:waste feed ratio and the gas

superficial velocity in the chlorinator. Other variations
were made in the facility when required for specific tests.

5   By way of examples of the results that
demonstrate our invention, the results of various tests are
given below. In each of these tests the waste material
containing the chlorides typically as listed in Table 1 was
fed into the dechlorinator with oxygen under controlled,
steady conditions. The products were analysed and the
10   percent chlorine recovery and carbon conversion (=100 x
chlorine or carbon transferred to the gas phase/chlorine or
carbon in the feed) were determined. The distribution of
residual carbon and chlorine among the condensed products
and gas were also determined. Typical results which
15   illustrate the effects of various parameters are given in
Tables 2-4.

       In tests 1 and 2, gas at a superficial velocity
of 0.5 m/s, calculated from the flow of oxygen in the
20   reactor at the reaction temperature, and a constant oxygen:
feed molar stoichiometric ratio of approximately 0.54 was
used and the effect of varying the temperature is shown in
Table 2. We show that the carbon combustion dropped
significantly from 58% to 16% when the temperature was
25   reduced from 615 to 600°C thereby producing a gas much
richer in chlorine. The results also show that the chlorine
recovery increased significantly with temperature with a
recovery of 85% obtained at 615°C.

30   In tests 3 and 4 the effect of increasing the
superficial velocity was investigated at constant
temperature and stoichiometric ratio. Again we demonstrate
in Table 3 that by increasing the superficial velocity the

carbon conversion was decreased to as low as 14% thereby
allowing a richer chlorine gas to be produced.

Table 2.   Effect of temperature

5

	Test 1	Test 2
Temperature (°C)	615	600
Gas superficial velocity (m/s)	0.5	0.5
Stoichiometric ratio	0.56	0.53
Chlorine recovery (%)	85	62
Carbon conversion (%)	58	16

Table 3. Effect of gas superficial velocity

	Test 3	Test 4
Temperature (°C)	600	600
Superficial velocity (m/s)	0.7	0.3
Stoichiometric ratio	0.75	0.71
Chlorine recovery (%)	69	85
Carbon conversion (%)	14	33

10

As a further illustration of the invention, the
results of tests 5 and 4 are compared in Table 4.   In this
case a constant temperature and superficial velocity were
maintained and increasing the stoichiometric ratio
15 increased the chlorine recovery to 85% and reduced the

carbon conversion from 36 to 33%, again leading to the
production of a richer chlorine gas.

Table 4. Effect of oxygen:waste (molar) stoichiometric
5   ratio

	Test 5	Test 4
Temperature (°C)	600	600
Superficial velocity (m/s)	0.3	0.3
Stoichiometric ratio	0.4	0.7
Chlorine recovery (%)	55	85
Carbon conversion (%)	36	33

        It should be emphasised that the results in
Tables 2-4 are only quoted by way of example to illustrate
10   that the invention gives us the ability to independently
control the carbon combustion and chlorine conversion to
produce chlorine gas of the desired concentration depending
on the application and usage of chlorine.

15   We have also demonstrated that the invention
provides a means for stripping the chloride coating from
the carbon particles during their residence in the
fluidised bed and that the unreacted carbon blown over and
collected in the cyclone is substantially free of chloride.
20   The chlorine from the chloride coating and separate
chloride particles react with the oxygen in the gas and
chlorine is efficiently separated from the carbon
particles.

By way of example, in Test 4, a low carbon conversion of 16% was obtained. Of the unconverted carbon, 88% was collected in the cyclone thereby achieving an

5 efficient separation of the carbon and only a small loss of carbon as carbon dioxide into the gas phase. In Tests 1 and 5, 95% and 89% respectively of the unreacted carbon was collected in the cyclone and confirm that the application of the invention results in good collection efficiencies of

10 the unreacted carbon in the cyclone. These examples are quoted to illustrate the invention and are not intended to be limiting in any way.

A further aspect of our invention is that it also

15 provides a means for increasing the chlorine recovery from the waste by separating the blown over carbon and rutile particles in the cyclone at a temperature above the condensation temperature of any unreacted chloride which avoids the condensation of these chlorides in the cyclone.

20 The temperature of the cyclone will depend on the type of chloride vapors in the exit of the dechlorinator. By maintaining the temperature of the cyclone above the condensation temperature of the vapors, the unreacted vapors are separated from the carbon and rutile particles.

25 For example a temperature of about 350°C ensures that ferric chloride vapour does not condense in the cyclone.

A further aspect of the invention is that the upper limit of the temperature of the cyclone is determined

30 by the need to prevent the oxidation of carbon in the cyclone. This will depend on several factors including the carbon content of the material collected in the cyclone, the oxygen potential of the gas, determined by its CO_2 and

oxygen concentration, the reactivity of the carbon in the gas and the residence time of particles and gas in the cyclone. In typical operation with a waste of the composition and characteristics in Table 1 we have found

5 that temperatures up to 400-450°C are very satisfactory to ensure negligible carbon oxidation. However, it should be emphasised that our claims are not limited to these temperatures due to the related considerations mentioned above.

10

We have also found that the unreacted chloride vapors can be condensed in an appropriately designed condenser to produce a condensed chloride product substantially free of carbon and rutile. The design

15 conditions for the condenser can be easily determined from the knowledge of the hot gas and vapour compositions and flow rates arriving at the quencher and the temperature which determine the amount of heat to be extracted to cool the gas and the surface area required to achieve efficient

20 condensation.

As a further aspect of our invention it is possible to treat this condensed product which is substantially chloride either by recirculating it to the

25 fluidised bed reactor or by treating it with oxygen in a separate reactor to increase the recovery of chlorine.

Our invention therefore relates to the novel processing steps which maximize the recovery of chlorine,

30 minimize the conversion of carbon, and separate the unconverted carbon and rutile and other inert materials from the waste in an appropriately designed cyclone.

The overall process is illustrated in the flow chart given in Fig 6. The process comprises feeding chlorinator waste with oxygen or an oxygen-containing gas to the fluidised bed dechlorinator in which the conditions

5   of temperature, gas velocity and oxygen: feed stoichiometry are controlled in an appropriate manner to optimise the recovery of chlorine and minimize the conversion of carbon. This dechlorination step essentially separates the chlorine from the chloride coating associated

10 with carbon and rutile particles contained in the chlorinator waste. A chlorine rich vapour stream leaves the dechlorinator and is passed to a cyclone in which any particles of carbon and rutile which leave the dechlorination reactor (having been stripped of chlorine in

15 the reactor) are separated from the gas stream. The cyclone is maintained at a temperature above the condensation temperature of any unreacted chlorides so that an effective separation is achieved between the solids and the unreacted chloride vapors. Any unreacted chloride

20 vapors remain in the chlorine-rich gas stream and are conveyed to the quencher. In the quencher any unreacted chlorides are condensed but the chlorine gas stream passes through the quencher to a baghouse to remove any residual fine dust particles so as to obtain a clean gas. The

25 quencher condenses chlorides, which are substantially free of carbon, rutile and other solids and may be recirculated to the dechlorination reactor or may be reacted separately with oxygen to recover the residual chlorine. Thus, the process offers a practical means of increasing the chlorine

30 recovery.

Throughout this specification and the claims, the words "comprise", "comprises" and "comprising" are used in a non-exclusive sense.

5   Modifications to the process for chlorine recovery described above apparent to the person skilled in the art and within the spirit and scope of the present invention are encompassed by the above description.

10

Dated this 7th day of July 1998
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION
By their Patent Attorneys
15   GRIFFITH HACK
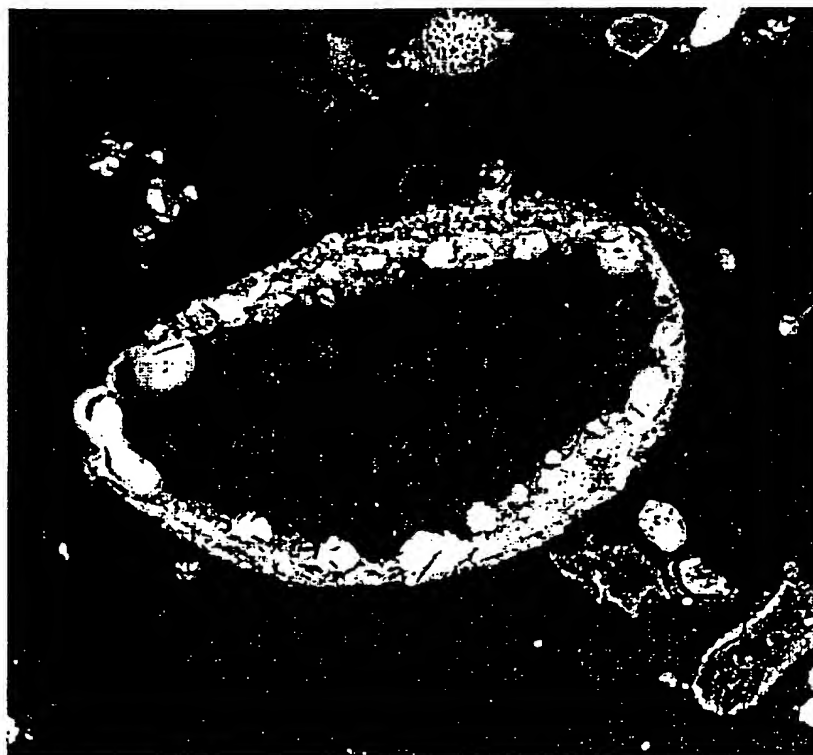Fellows Institute of Patent
Attorneys of Australia

TiO₂
Raw Pigment

O₂

Oxidation

TiCl₄

Purification

Cl₂ for recycle

TiCl₄

Dechlorination

FeCl₂

Condensation

Recycled
Cl₂

dry
Fe₂O₃

Chlorinator
Waste

O₂

TiCl₄
FeCl₂

Synthetic
Rutile

Chlorination

Fresh
Cl₂

C

FIG 1

100 μm (a)

100 μm (b)

FIG 2

FIG 3

FIG 4

FIG 5

Dechlorinator

Waste and oxygen feed

Bed overflow solids

Cyclone solids

Cyclone

Quencher

Quencher solids

Chlorine containing gas

Baghouse

Baghouse solids

FIG 6